OBSERVATIONS ON THE HYPOPHOSPHATES OF THORIUM AND THE RARE EARTHS

BY

GLADYS HELEN QUINTY

B.S., University of Illinois, 1946

AN ABSTRACT OF A THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN CHEMISTRY
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OBSERVATIONS ON THE HYPOPHOSPHATES OF THORIUM AND THE RARE EARTHS

I. Introduction

Thorium hypophosphate was first described by Kauffman (1) in 1899. The compound received immediate attention because of its exceedingly slight solubility in both dilute and concentrated acids and alkali. The possibility of using this compound for quantitative separations was recognized when it was reported that the rare earth hypophosphates were soluble at comparatively low acid concentrations.

A radiometric method of analysis for determining thorium in the presence of the rare earths was developed recently by Moeller and Schweitzer (2). The procedure is based upon the precipitation of thorium from solutions 0.3 *N* in acid by the addition of a known amount of standard radioactive pyrophosphate solution. The radioactivity removed from the solution is proportional to the quantity of thorium in the sample. The usefulness of the procedure is limited since the pH of the solution must be carefully controlled in order to effect clean-cut separations from the other substances present in the solution. A consideration of the chemistry of hypophosphoric acid and its salts suggested that the precipitation of thorium as the hypophosphate might also be made the basis of a similar radiometric method.

Before undertaking the actual investigation of the radiometric procedure for analysis, preliminary studies on the thorium and rare earth hypophosphates were carried out. It was necessary to prepare the compounds, to verify their compositions, to determine their relative solubilities, and, also, to establish the approximate pH values at which the compounds precipitate. In addition, it became obvious during the course of the investigation that adsorption and peptization phenomena were causing difficulties in the procedure. Therefore, the colloidal properties of these compounds were also studied.

II. Materials And Apparatus

The rare earth materials used in this investigation were obtained from the stock of the Division of Inorganic Chemistry at the University of Illinois. Disodium hypophosphate was prepared by treating sodium chlorite solution with red phosphorus according to the method outlined by Leininger and Chulski(3). The radioactive phosphorus-32 was obtained from the Oak Ridge National Laboratories, Oak Ridge, Tennessee. All other chemicals were commercially available and, in general, of analytical reagent grade.

Several instruments were used: (1) a Geiger-Müller counter, an impulse register, a quenching circuit, and a cylindrical counting tube, (2) a Beckman Model G pH Meter, the glass electrode of which was calibrated frequently against standard buffer, and (3) a Leeds and Northrup A. C. Conductance Bridge.

III. Experimental And Results

A. Preliminary Investigations on Rare Earth and Thorium Hypophosphates

Thorium, yttrium, and neodymium hypophosphates were prepared by treating solutions of the salts of these metals with solutions of disodium hypophosphate. X-ray powder patterns showed that the yttrium and neodymium compounds were crystalline materials. Thorium hypophosphate precipitates, however, were not crystalline even after long periods of digestion.

Two procedures were found to be useful for the determination of the compositions of these compounds. Conductometric titrations indicated that the thorium compound corresponds to the formula, ThP_2O_6, whereas the neodymium and yttrium compounds are represented by $(R.E.)_4(P_2O_6)_3$. A wet chemical method based upon the oxidation of hypophosphate to orthophosphate was developed for determining the composition of thorium hypophosphate. Thorium hypophos-

phate precipitates were dissolved in a solution of cerium(IV) in 1 *N* nitric acid. The quantity of cerium solution in excess was determined by titrating potentiometrically with a standard arsenite solution using a trace of osmic acid as the catalyst. The amount of hypophosphate in the compound was calculated from the quantity of cerium used in the oxidation. The thorium in solution was precipitated, along with the cerium, as the oxalate and was ignited to the oxide. Since the weight of cerium in the mixed oxides was known, the amount of thorium was determined. The results showed that thorium and hypophosphate react in a 1 to 1 mole ratio. The procedure was modified to permit the analyses of the yttrium and neodymium compounds since these were not soluble in the nitratocerate solutions. The compounds were first dissolved in a minimum of concentrated nitric acid and this solution was treated with the standard cerium solution. Cerium hypophosphate was precipitated but was dissolved when the suspensions were heated. Neodymium-hypophosphate ratios of 4.8 to 3 and yttrium-hypophosphate ratios of 4.6 to 3 were found. The deviations were attributed to the precipitation of the rare earth phosphates along with the oxalates.

B. Radiometric Studies

It was shown from solubility studies that the separation of thorium from the rare earths as the hypophosphate is possible in 4 *N* hydrochloric acid solution. Therefore, a radiometric method for determining thorium using hypophosphate was investigated Analyses for thorium were run on pure thorium solutions with a radioactive hypophosphate solution. It was found that in low thorium concentrations, 9 mg. or less per fifty milliliters of solution, the thorium detected was less than that added. In concentrations greater than this, the thorium detected was greater than that added. Errors approaching 18% were noted. The addition of electrolyte had little effect on these values. Heating the samples at various temperatures magnified the errors in the low concentrations, and it was found that, when samples were heated at 85°C. for three hours, low results were observed for those containing

less than 35 mg. of thorium. In greater concentrations, high results were again obtained but to a lesser extent (approaching 5%).

Experiments showed that the thorium hypophosphate precipitates adsorbed hypophosphate ion. The relationship between the adsorption and the quantity of thorium precipitated was studied, and it was found that a log-log plot of the thorium concentration against the hypophosphate adsorbed was linear within the region investigated.

C. Colloidal Characteristics of Thorium Hypophosphate

Thorium hypophosphate colloids were formed when hypophosphate precipitates suspended in acidic solutions were treated with large quantities of thorium salt solutions. These colloidal systems were studied in the ultracentrifuge, and calculations using the classical equations of Svedberg showed that the average diameter of these particles prepared under the given set of conditions was 30 A. It was also observed that, when thorium nitrate solutions were run in the ultracentrifuge between 29,000 and 50,000 r.p.m., the thorium ion was sedimented appreciably. The observed sedimentation was very nearly that calculated from the classical ultracentrifuge equations.

IV. Summary

Thorium, yttrium, and neodymium hypophosphates were prepared and their compositions were determined. A radiometric method for determining thorium in the presence of the rare earths was investigated. The method involved the precipitation of thorium as the hypophosphate from solutions 4 *N* in acid. However, the method was not successful since the thorium hypophosphate precipitates strongly adsorbed hypophosphate ion. The colloidal characteristics of thorium hypophosphate were also investigated. Ultracentrifuge studies indicated that the average particle size of the colloidal particles was 30 A. It was also found that thorium ion was

appreciably sedimented in the ultracentrifuge.

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VITA

Gladys Helen Quinty was born on September 3, 1924 in Trenton, New Jersey. She received her elementary and high school education in the public schools of that city, graduating from Trenton Central High School in 1942. In September of that year, she entered Albright College in Reading, Pennsylvania. After completing two years work, she transferred to the University of Illinois in September, 1944, from which institution she was graduated with the degree of Bachelor of Science with High Honors in June, 1946. She was employed by E. R. Squibb and Sons in New Brunswick, New Jersey from July, 1946 until she entered the Graduate College of the University of Illinois in February, 1948. She held an appointment as half time teaching assistant in inorganic chemistry from February, 1948 to June, 1948. From that time until June, 1950, she was a research assistant on the University of Illinois Rare Earth Research Program sponsored by the Office of Naval Research. During the academic year 1950-1951, she held a University of Illinois Fellowship in Chemistry.

The author is a member of the American Chemical Society, Iota Sigma Pi, Sigma Delta Epsilon and Sigma Xi.

She is joint author of the following publication:

Moeller, T. and Quinty, G. H. "Spectrophotometric Studies on Colloidal "Lanthanum Blue", J. Phys. Chem. 59, 315 (1950)